Determination of Irganox 1010 in polyethylene by infrared spectroscopy

Analytical method

Polymers

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Scope

This method is for the determination of Irganox 1010 and chemically identical antioxidants in polyethylene where the additive package is known. The method utilizes a characteristic ester carbonyl band associated with the additive that is common in many other additives. Therefore, the total additive package must be known to confirm that other additives present do not contain bands that would interfere with the measurement. The method is typically used for process control of additive addition and is not recommended for filled or pigmented resins. The sample must be pressed into a film or coupon prior to the analysis.

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Summary

An analytically representative sample of the polyethylene resin is molded into a 0.5 to 0.7 mm thickness film. Molding conditions are not important to the results obtained by this method, as long as the resin is not subjected to temperatures of more than 250 °C for more than 2 to 3 minutes, and the films have a smooth, consistent surface. The film is placed in the infrared spectrometer to obtain the spectrum at 4 wavenumber resolution or better. Using the Agilent DialPath or TumbIIR accessories, the film or coupon can be inserted into the infrared beam path between the top and bottom crystals (Figure 1). Both these accessories are unique to Agilent and provide a revolutionary new way to measure thin polymer films or liquids. The horizontal mounting provides a simple, fast and reproducible mechanism to mount the sample by simply laying it down flat and rotating the crystal into position, eliminating errors and providing accurate and reliable answers — fast! The absorbance of the additive band is measured at 1745 cm^{-1} and the absorbance is measured for the reference band at 2019 cm^{-1} to provide a path length or film thickness correction. To obtain the additive concentration in the sample, the ratio of the additive band to the reference band is substituted into a linear regression calibration equation constructed from measurements of prepared standards with known concentrations of additive. Triplicate films are averaged to obtain a result.

Figure 1. The Agilent DialPath transmission cell used for polymer analysis of coupons or films

Apparatus

- Data is obtained using an Agilent Cary 630 FTIR spectrometer equipped with a DialPath or TumbIIR sample interface with a 1000 µm path length. Equivalent FTIR spectrometers, such as the mobile or portable Agilent 5500/4500 Series FTIR, can also be used.
- Film micrometer — capable of measuring 0.5–0.7 mm thickness.
- Hydraulic press — with heated platens capable of maintaining 200 °C and a ram force of 40,000 pounds.
- Chase mold — to control thickness.
- Aluminum sheet — 0.051–0.178 mm thick.
- Scissors.

Calibration

Standards are prepared by blending known amounts of Irganox 1010 with polyethylene powder, and compounding under a nitrogen blanket until thoroughly mixed.

To perform the calibration, prepare and analyze at least three films for each standard resin in accordance with the requirements of this method. Perform a linear least squares regression of the concentration of the analyte versus normalized absorbance using all data points; do not include the origin as a data point.

$$Wt\%\ Irganox\ 1010 = M \times (A_{1745}/A_{2019}) + N$$

Where:

Wt% Irganox 1010	= Weight % of Irganox 1010 in the polyethylene
A_{1745}	= Absorbance of Irganox 1010 at 1745 cm^{-1}
A_{2019}	= Absorbance of polyethylene reference band at 2019 cm^{-1}
M	= Calibration constant
N	= Intercept

The calibration curve for the determination of Irganox 1010 in polyethylene for the standards used in this study is shown in Figure 2.

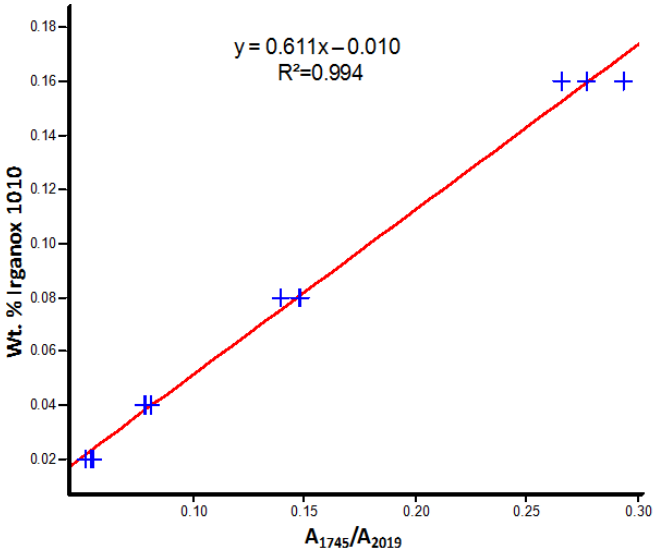

Figure 2. Calibration curve for wt% Irganox 1010 in polyethylene

Procedure

Sample preparation

Molding techniques and conditions used to prepare the sample do not significantly influence the results, as long as the resin is not subjected to temperatures of more than 250 °C for more than 2 to 3 minutes, and the prepared films have a smooth, consistent surface. A typical preparation procedure is as follows:

Obtain a representative sample of the resin to be analyzed; statistical sampling techniques are recommended (cone and quarter technique, chute splitter, rotary splitter, roto-riffler, and so forth). Place the chase mold on a sheet of aluminum and slightly overfill each cavity in the chase with the resin. Another sheet of aluminum is placed on top and the stack is carefully placed in the press with the platens heated to 200 °C. The press is closed to apply minimal force for 1 or 2 minutes while the sample melts. The force is increased to at least 25,000 pounds, held for approximately 30 seconds, and released. The stack is then removed from the press and allowed to cool on the benchtop. The aluminum sheet is stripped from the chase and the films are pushed from the cavities and trimmed to remove the flash. Examine the sample for surface defects and check to ensure that the thickness is between 0.5 and 0.7 mm. Samples with defects or thickness outside of the range are discarded; at least three suitable films are required for the analysis.

Operating conditions

The infrared spectrometer should be turned on for at least 15 minutes prior to analysis. The resolution should be set to at least 4 wavenumbers.

Collect for a minimum of 30 seconds (70 scans) for each of the triplicate film samples.

Method configuration

To determine the additive concentration, measure the area under the absorbance band for Irganox 1010 at 1745 cm^{-1} relative to a baseline drawn between 1775 and 1706 cm^{-1}. The specified peak areas and baseline points can easily be set in an Agilent MicroLab PC FTIR software method. Each peak measurement is called a component and the baseline limits are easily set as shown in Figure 3. The peak type of 'Peak Area with Duel Baseline' is first set. Then parameters for measurement of the area under the reference polyethylene absorbance band at 2019 cm^{-1} relative to a baseline drawn between 2108 and 1981 cm^{-1} (Figure 4) are set. The component is further configured to report the absorbance value to five decimal places as shown in Figures 3 and 4.

A ratio of the analyte band absorbance to the reference band is used for this analysis.

$$\text{Wt\% Irganox 1010} = M \times (A_{1745}/A_{2019}) + N$$

with M and N as determined in the the Calibration section.

The MicroLab PC FTIR software makes the peak ratio calculation easy to set up. Simply edit the method by selecting the 'Peak Ratio' calculation type and the peak components that are to be ratioed (Figure 5).

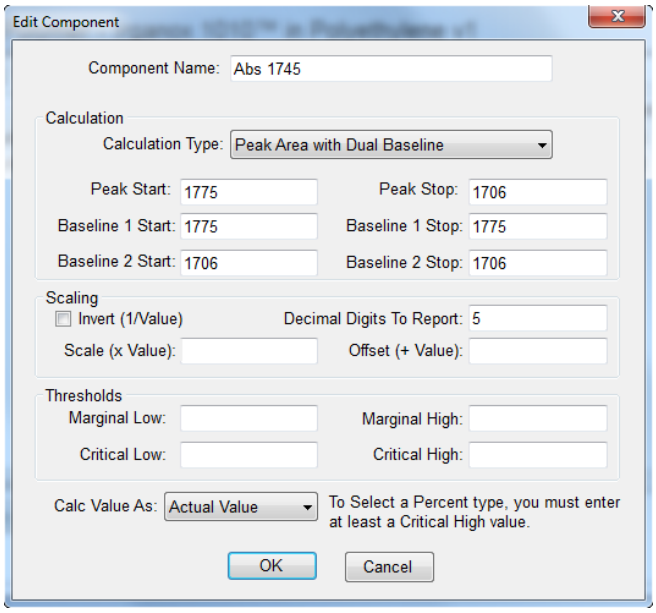

Figure 3. The Irganox 1010 peak area absorbance (component) measurement at 1745 cm^{-1} in the MicroLab PC FTIR software. The peak start and stop refers to the area under the peak to be integrated. Single point baselines should be set up with the same baseline start and stop points.

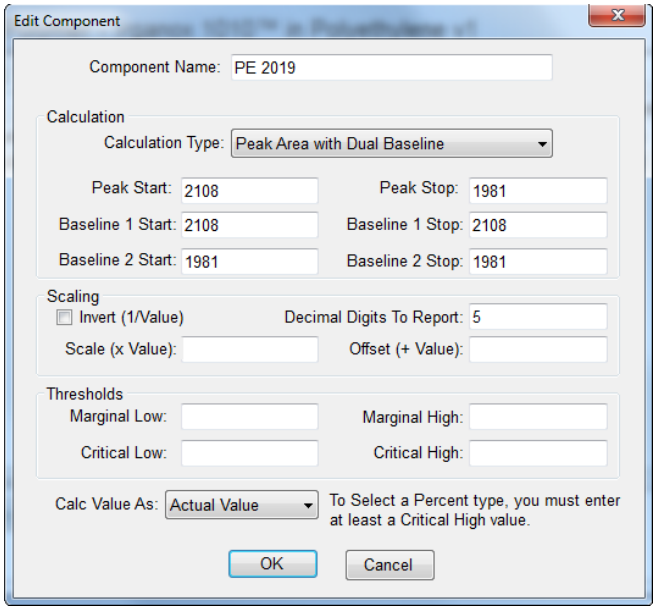

Figure 4. The polyethylene reference peak component addition in the MicroLab PC FTIR software

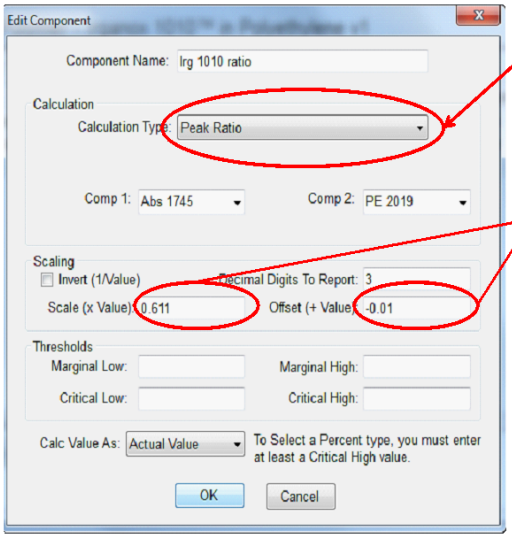

Figure 5. The peak ratio component addition in the MicroLab PC FTIR software. After plotting the calibration data, the resulting linear regression line's slope is entered in the 'Scale' field and the Y-axis offset in the 'Offset' field.

Analysis

With the ratio defined, the new method is ready to be used to obtain at least triplicate measurements of each calibration standard. Unknown polymer coupons should also be run with a minimum of three measurements around the coupon. This process is made simple and convenient with the DialPath or TumblIR transmission cells. Users can see the exact point of measurement in real time, and quickly reposition the sample for the replicate measurements.

Plot the values measured for the ratio relative to the Irganox 1010 concentration (Figure 2), and insert the slope and offset values back into the method as shown in Figure 5. Once the slope and offset values have been entered, the Microlab PC FTIR software method will report the Irganox 1010 concentration.

The MicroLab PC software method, Polymer — Irganox 1010 in Polyethylene v1, includes the calibration data from Figure 2. This calibrated method is available with the Agilent 5500 and 4500 Series DialPath or TumblIR FTIR spectrometers, as well as the Cary 630 FTIR spectrometers. This method and software performs all the calculations automatically and reports the final value as wt% Irganox 1010 (Figure 6).

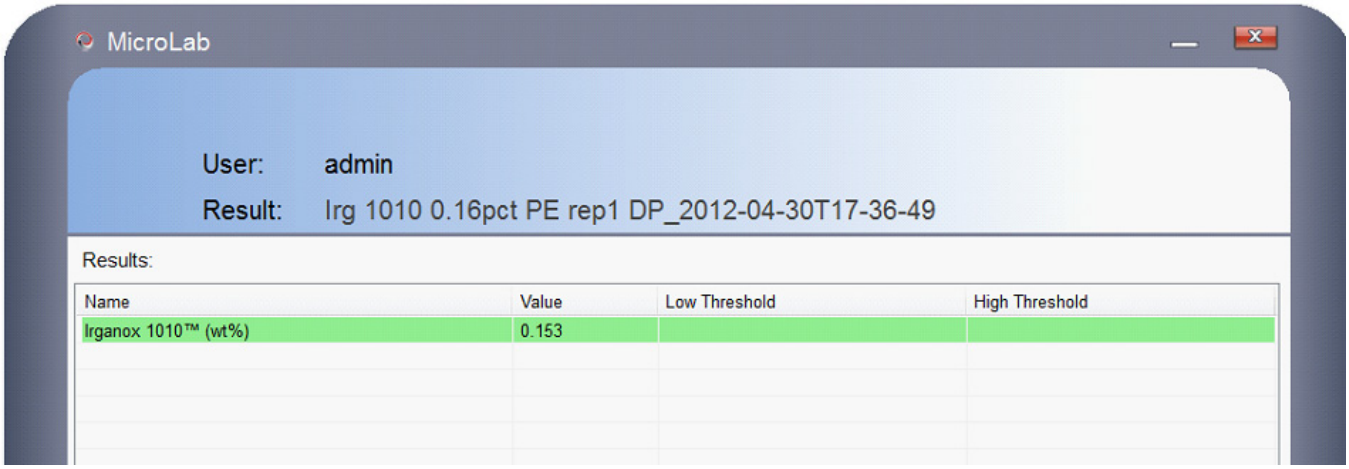

Figure 6. The MicroLab PC FTIR software prediction result for a 0.16 wt% Irganox 1010 in polyethylene sample

The values obtained from triplicate determinations should be averaged to give the final reported concentration.

Conclusion

This analytical method demonstrates how the Agilent Cary 630 FTIR can be used to easily and accurately measure polymer thin films. The unique sampling capabilities of the DialPath and TumbIIR provide a simple mechanism to mount your sample, while the step-by-step method-driven software with color-coded, actionable results guides you through your analysis to ensure that your samples are measured with minimum effort and highest accuracy.

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